

B.Sc IV Semester

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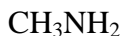
Associate Prof.

Chemistry deptt.

Amines

Amines are the organic compounds derived from ammonia (NH_3) by replacing its one or more hydrogen atoms by alkyl or aryl group.

For example:



Methyl Amine



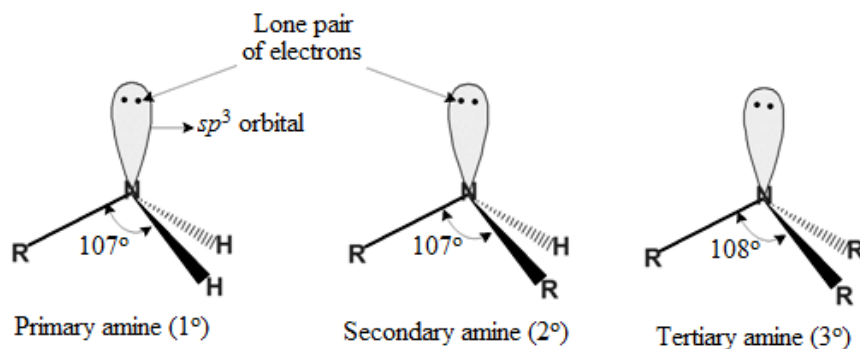
Ethyl Amine



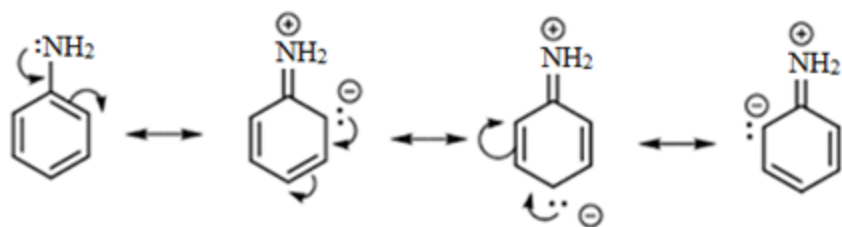
Aniline

Structure of Amines

Nitrogen atom of amines carries an unshared pair of electrons and is sp^3 hybridized with pyramidal shape. Due to the presence of unshared pair of electrons, the angle C–N–E, (where E is C or H) is less than 109.5° .



In aromatic amines, the C–N bond is slightly stronger due to the partial double bond character which arises as a result of delocalization of lone pair of N with the benzene ring.

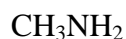


Classification of Amines

On the basis of number of hydrogen atoms replaced in NH_3 molecule, amines are categorized into three types:

- 1° amine: One hydrogen atom of NH_3 is replaced by an alkyl or aryl group.

For example:



Methyl Amine

- 2° amine: Two hydrogen atoms of NH_3 are replaced by alkyl or aryl groups.

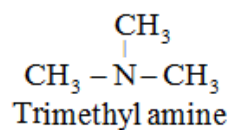
For example:



Dimethyl Amine

- 3° amine: All three hydrogen atoms of NH_3 are replaced by alkyl or aryl groups.

For example:

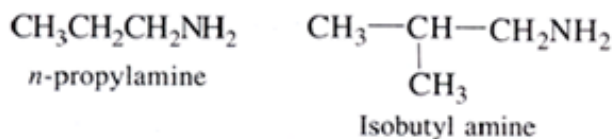


Nomenclature of Amines

Common naming system:

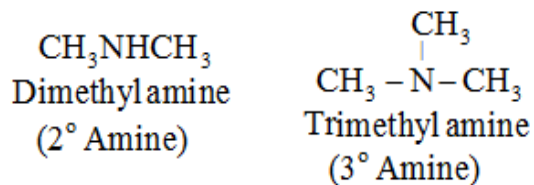
- Aliphatic amines are named by prefixing an alkyl group to a mine, i.e., alkylamine.

For example:



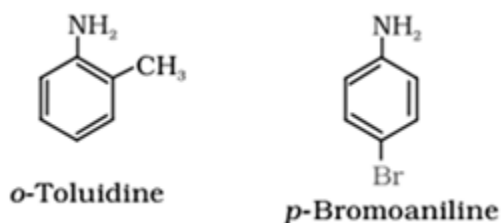
- Secondary and tertiary amines, having two or more similar groups are named by adding prefix 'di' or 'tri' before the name of alkyl group.

For example:



- Aromatic amines are named as derivatives of the parent member, aniline ($\text{C}_6\text{H}_5\text{NH}_2$).

For example:



IUPAC naming system:

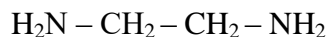
- Aliphatic or aromatic amines are named by replacing 'e' in the end of the parent hydrocarbon by 'amine'.

For example:



- Amines containing more than one amino groups at different positions in the parent chain, are named by specifying numbers to the carbon atoms bearing $-\text{NH}_2$ groups along with attaching a suitable prefix such as di, tri, etc. to the amine. The ending 'e' of the hydrocarbon is retained.

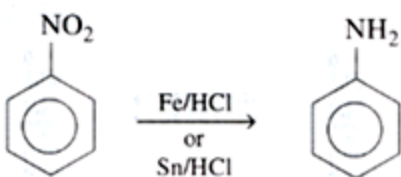
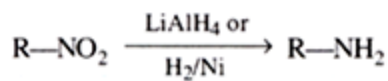
For example:



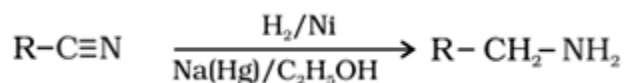
Ethane-1, 2-diamine

Preparation of Amines

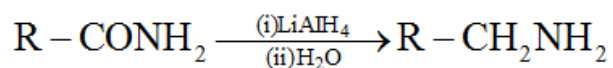
1. By reduction of nitro (RNO_2) compounds:



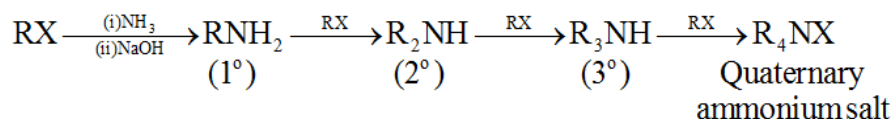
2. *By reduction of nitriles (RCN):*



3. *By reduction of amides (RCONH₂):*



4. *By ammonolysis of alkyl halides:*

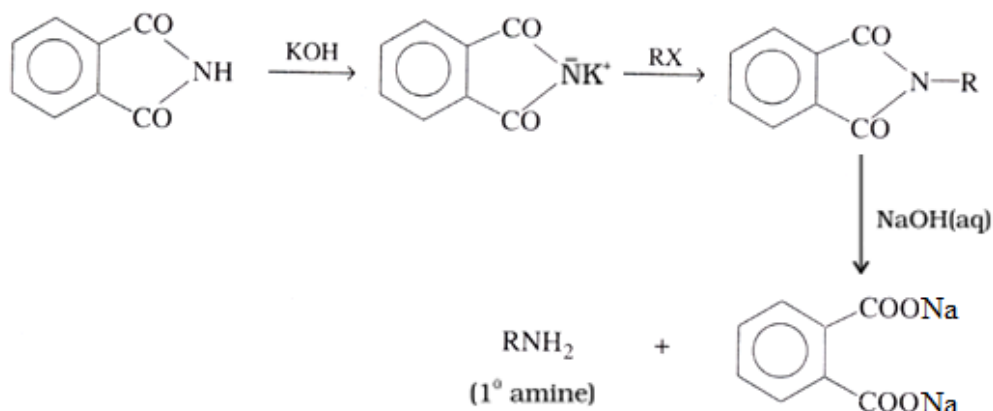


5. *Hofmann bromamide reaction:*



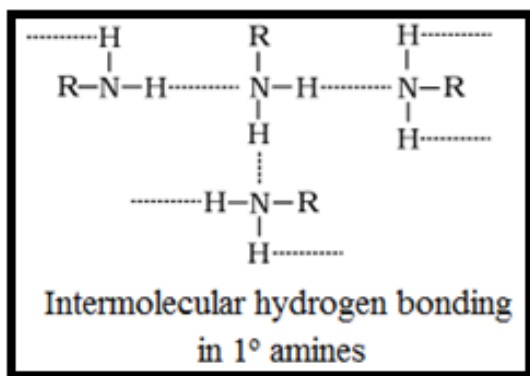
This method gives amine with one carbon less than the parent amide.

6. *Gabriel phthalimide synthesis:*



Physical Properties of Amines

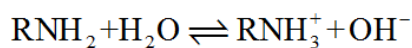
- The lower aliphatic amines are gases with fishy smell.
- Primary amines with three or more carbon atoms are liquid and higher members are all solids.
- Lower amines are soluble in water as they can form hydrogen bonds with water, however the solubility decreases with increase in hydrophobic alkyl group.
- Amines have a higher boiling point than the hydrocarbon of comparable molecular mass. This is due to their ability to associate via intermolecular hydrogen bonding.



- Boiling points order of various isomeric amines is:
 $1^\circ > 2^\circ > 3^\circ$

Basic strength of amines

Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom. Basic character of amines can be better expressed in terms of their K_b and pK_b values.



$$k_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

$$\text{Basicity} \propto K_b \propto \frac{1}{pK_b}$$

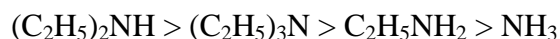
$$\text{Where, } pK_b = -\log K_b$$

All aliphatic amines are strong bases than NH_3 while aromatic amines are weaker bases than NH_3 due to the electron withdrawing nature of the aryl group.

Factors affects the basicity of aliphatic amines are:

- Inductive effect
- Solvation effect
- Steric hinderance

Considering all the above factors the basic strength of methyl substituted amines and ethyl substituted amines in aqueous medium follows the order:



Basicity of amines

Basicity of aliphatic amines

In amines, there is a lone pair of electrons on nitrogen. The tendency of nitrogen to share these electrons with acids is responsible for the basic character of amines.

For comparison of the basic character of amines, the equilibrium constant of following reaction is a measure of their basic character.

Since $[\text{H}_2\text{O}]$ is constant

The basicity constant $K_b = K_{\text{eq}} [\text{H}_2\text{O}]$

Aliphatic amines with K_b between 10^{-3} and 10^{-4} are stronger bases than ammonia ($K_b = 1.8 \times 10^{-5}$).

Like ammonia, amines are strong bases and react with mineral acids to form ammonium salts from which they can be liberated by treatment with a strong base like NaOH.

That alkylamines are stronger bases than ammonia can be expressed in terms of electron releasing inductive effect of alkyl groups. Alkyl groups by their electron releasing effect, concentrate electron density on nitrogen and hence make the lone pair of nitrogen more easily available for sharing with acids. Also the electron releasing effect of alkyl groups stabilizes the alkyl ammonium ion formed and hence shifts the equilibrium in forward direction making the alkylamines stronger bases than ammonia.

Thus the basic character of aliphatic amines should increase with increase of alkyl substitution. In the gas phase, the basic trend in nature is as expected i.e.,

tertiary amine > secondary amine > primary amine > ammonia.

The order of basicity in aqueous solution

However, the order of basicity in aqueous solution does not follow the expected trend and gets altered as revealed by their K_b values.

The basic strength in aqueous solution depends not only upon electron releasing effect but also upon steric effect and hydration effect.

a) Steric effect

Steric effect refers to the crowding of alkyl groups around N atom which hinders the attack of proton on the amine molecule and this decreases its basic strength. Since crowding of alkyl groups around N atom increases from 1° to 3° amines, the basic strength of amine should decrease in the order $1^\circ > 2^\circ > 3^\circ$.

b) Hydration effect

Hydration effect refers to the stabilization of the protonated amine by water molecules. The water molecules form H - bonds with the protonated amine and release energy called hydration energy.

Greater the extent of H - bonding in protonated amine more will be its stabilization and consequently greater will be the basic strength of the corresponding amine.

Hydration due to hydrogen-bonding is maximum in monoalkyl ammonium ion (protonated cation of 1° amine), it is less in dialkyl ammonia ion and still less in trialkyl ammonium ion. Thus basic strength should decrease from $1^\circ > 2^\circ > 3^\circ$.

In 3° amine, hydration is least, steric hinderance is maximum so least basic in spite of maximum inductive effect.

In 1° amine, steric hinderance is least, hydration is maximum and inductive effect is minimum. So its basic strength is more than 3° amine.

The resultant of all factors cause 2° amine to be still more basic than 1° amine.

So overall basic strength varies as $2^\circ > 1^\circ > 3^\circ$.

Basicity of aromatic Amines

Aromatic amines are less basic than aliphatic amines and ammonia. Reason: - • pK_b value of aniline (pK_b: 9.4) is quite higher than ammonia (pK_b: 4.7). It is because in aniline or other arylamines, the -NH₂ group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation (The lone pair of electrons on the nitrogen atom is delocalised into the benzene ring on to the ortho and para positions) with the benzene ring and thus making it less available for protonation.

Effect of substituents on the basicity of amines

The basicity of amines of different classes do not follow a simple pattern because the number of groups bonded to nitrogen affects the electron density at the nitrogen atom. The basicity of an amine is increased by electron-donating groups and decreased by electron-withdrawing groups. Aryl amines are less basic than alkyl-substituted amines because some electron density provided by the nitrogen atom is distributed throughout the aromatic ring.